

AMMONIUM POLYPHOSPHATE SOLUTIONS CONTAINING MULTI-FUNCTIONAL
PHOSPHONATE CORROSION INHIBITORS

STATEMENT REGARDING FEDERALLY FUNDED RESEARCH OR DEVELOPMENT

Not applicable.

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of U.S. Patent Application Serial Number 09/723,567,
filed November 28, 2000, which is hereby incorporated by reference in its entirety.

REFERENCE TO MICROFICHE APPENDIX

Not applicable.

FIELD OF THE INVENTION

The present invention relates to ammonium polyphosphate solutions. More
specifically, the present invention relates to ammonium polyphosphate solutions containing
iron additives and water soluble phosphonates for reduced aluminum corrosion.

BACKGROUND OF THE INVENTION

Aerial application of fire-retardant compositions to combat the spread of wildland fires
is common. The composition of fire retardant concentrates designed for managing and
controlling wildland fires are of two generally types, those which, when mixed or diluted with
water to end-use concentration, result in either a gum thickened solution, and those which do
not contain a gum thickener and, consequently, result in water-like solutions, which are not
rheologically modified. These water-like retardant solutions exhibit inferior drop
characteristics. The former may be supplied as dry powders or as suspensions or slurries,
which are generally referred to as fluids. Those concentrates that result in water-like solutions
when diluted with water may contain suspended components, as well, but are generally
referred to as liquid concentrates. Fire retardant concentrates that are supplied as fluids or

liquids are preferred by some because they can be simply and easily diluted to end-use strength with little mixing hardware and manpower.

Fertilizer grade ammonium polyphosphate liquids have been used as aerially applied fire-retardants. These liquids have certain advantages in comparison to other fire-suppressing compositions since they can be transported and stored prior to use in the liquid form rather than being mixed from dry ingredients. However, concentrated liquid fire retardants and solutions prepared therefrom are extremely corrosive to aluminum and brass and mildly corrosive to other materials of construction used in handling, storage and application equipment. As used herein, all metals include alloys thereof. Accordingly, aluminum includes aluminum 2024T3, 6061 and 7074, steel includes 1010 and 4130 steel and brass includes yellow and naval brass. Since wildland fire retardants are most frequently transported to the fire and applied aerially, it is imperative that corrosive damage to the materials of construction of fixed-wing aircraft and helicopters be minimized.

Accordingly, the United States Department of Agriculture ("USDA") Forest Service has established, in "Specification 5100-304b (January 2000) Superseding Specification 5100-00304a (February 1986)," entitled "Specification for Long Term Retardant, Wildland Fire, Aircraft or Ground Application" (hereinafter, "Forest Service Specifications"), hereby incorporated by reference in its entirety, maximum allowable corrosion rates for 2024T3 aluminum, 4130 steel, yellow brass and Az-31-B magnesium. For example, the corrosivity of forest fire retardants, in concentrate, to aluminum, steel and yellow brass must not exceed 5.0 milli-inches ("mils") per year as determined by the "Uniform Corrosion" test set forth in Section 4.3.5.1 of the aforementioned USDA, Forest Service Specifications. If the product is applied from fixed-tank equipped helicopters, the corrosivity of the fire retardants to magnesium must not exceed 5.0 mils per year. The Forest Service Specifications identify the maximum amount of corrosion acceptable when both the retardant concentrate and its diluted

solutions are exposed to each metal indicated above at temperatures of 70° Fahrenheit ("F") and 120°F in both totally and partially immersed configurations. The maximum allowable corrosivity of aerially applied fire retardant diluted solutions to aluminum is 2.0 mils per year ("mpy"), and the maximum corrosivity to brass and steel is 5.0 mpy when partially immersed, and 2.0 mpy when tested in the partially immersed condition. In the partially immersed configuration, one-half of the coupon is within the solution and one-half is exposed to the vapors in the air space over the solution.

In an effort to address the corrosivity problems encountered with the use of fertilizer grade ammonium polyphosphates, sodium ferrocyanide was incorporated into the corrosive compositions. Sodium ferrocyanide has proven to be an effective corrosion inhibitor in fire retardant compositions containing ammonium polyphosphate fertilizer solutions. While sodium ferrocyanide is effective as a corrosion inhibitor, several disadvantages of its use make its incorporation into wildland fire retardant compositions undesirable. Specifically, the environmental and toxicological safety of ferro(i)cyanides is, at best, questionable. When exposed to acidic conditions and/or ultraviolet radiation from natural sunlight, the ferro(i)cyanide radical readily degrades releasing free iron and cyanide and/or hydrogen cyanide, which are toxic to humans, animals and aquatic life. Further, free iron emanating either from decomposition of a portion of the ferro(i)cyanide radical, or introduced from other components or impurities within the composition, will subsequently react with remaining non-decomposed ferro(i)cyanide to form ferrous ferricyanide ("Turnbull's Blue") or ferric ferrocyanide ("Prussian Blue"), which emit a persistent blue-black or indigo-blue coloration, staining all that they contact. Consequently, neither ferricyanide nor ferrocyanide can be used in fire-retardants that are expected to fade and become non-visible over time, for example, in fugitive retardant compositions.

The magnitude of the above concerns is increased since wildland fire retardants are generally applied aerially in a less than completely controlled manner. Due to the presence of variables such as vegetative cover, smoke, or wind drift that impact the trajectory of the free-falling solution, aerially applied wildland fire retardant solutions may land on or near people, animals and in bodies of water, or on soil where it could enter the water supply.

Accordingly, there is a need to provide safe and acceptable wildland fire retardants for the suppression or management of wildland fires that are not corrosive to the equipment associated with the transportation, handling and application of the retardant, have favorable rheological and aerial application characteristics and are environmentally and toxicologically friendly, thereby avoiding the above disadvantages.

SUMMARY OF THE INVENTION

In accordance with the objects of the invention, novel compositions and methods are provided. In a first aspect of the invention, a corrosion-inhibited fire retardant composition comprising at least one fire retardant composition comprised of at least one ammonium polyphosphate, at least one suspending agent, at least one phosphonate selected from a group consisting of aminotri(methylenephosphonic acid), 1-hydroxyethylidene-1,1-diphosphonic acid, hexamethylenediaminetetra(methylenephosphonic acid), diethylenetriaminepenta(methylenephosphonic acid), salts thereof, and mixtures thereof and a corrosion inhibiting system comprised of at least one corrosion inhibiting compound selected from a group consisting of azoles, insoluble ferric pyrophosphate, soluble ferric pyrophosphate, ferrous oxalate, ferric citrate, ferrous sulfate, ferric ammonium citrate, insoluble ferric orthophosphate, soluble ferric orthophosphate, ferric ammonium oxalate, ferric ammonium sulfate, ferric bromide, ferric sodium oxalate, ferric stearate, ferric sulfate, ferrous acetate, ferrous ammonium sulfate, ferrous bromide, ferrous gluconate, ferrous iodide, ferric acetate, ferric fluoroborate, ferric hydroxide, ferric oleate, ferrous fumarate, ferrous oxalate, ferrous

oxide, ferric lactate, ferric resinate, and any combination thereof. The corrosion inhibiting system is present in a minor amount effective to substantially reduce corrosiveness of said fire retardant composition.

In a second aspect of the invention, a method of preparing a corrosion-inhibited fire retardant composition, adapted for application to wildland fires, is provided that comprises forming an intermediate concentrate composition comprising the above-described corrosion-inhibited fire retardant composition, and diluting the intermediate concentrate with water to form the corrosion-inhibited fire retardant composition of the invention.

In a third aspect of the invention, a method of suppressing wildland fires comprising applying to wildland vegetation a fire suppressing composition comprising the above-described corrosion-inhibited fire retardant composition and water is provided.

In a fourth aspect of the invention, a method of inhibiting corrosion comprising providing a corrodible material, and contacting the corrodible material with the above-described corrosion-inhibited composition is provided.

In a fifth aspect of the invention, a corrosion-inhibited agricultural plant nutrient is provided that comprises at least one agricultural plant nutrient, at least one suspending agent, at least one phosphonate selected from a group consisting of aminotri(methylenephosphonic acid), 1-hydroxyethylidene-1,1-diphosphonic acid, hexamethylenediaminetetra(methylenephosphonic acid), diethylenetriaminepenta(methylenephosphonic acid), salts thereof, and mixtures thereof and a corrosion inhibiting system comprised of at least one corrosion inhibiting compound selected from a group of corrosion inhibiting compounds consisting of azoles, insoluble ferric pyrophosphate, soluble ferric pyrophosphate, ferrous oxalate, ferric citrate, ferrous sulfate, ferric ammonium citrate, insoluble ferric orthophosphate, soluble ferric orthophosphate, ferric ammonium oxalate, ferric ammonium sulfate, ferric bromide, ferric sodium oxalate, ferric

stearate, ferric sulfate, ferrous acetate, ferrous ammonium sulfate, ferrous bromide, ferrous gluconate, ferrous iodide, ferric acetate, ferric fluoroborate, ferric hydroxide, ferric oleate, ferrous fumarate, ferrous oxalate, ferrous oxide, ferric lactate, ferric resinate, and any combination thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

Not applicable.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In accordance with the present invention, it has been discovered that a fire-retardant composition can be prepared that has a reduced tendency to corrode various metals, including aluminum, that is superior to known fire retardants in rheological aerial application characteristics and is toxicologically and environmentally safe. The corrosion-inhibited fire retardants of the invention include at least one fire retardant composition comprised of at least one ammonium polyphosphate, at least one novel phosphonate, or salt thereof, at least one suspending agent, and a corrosion inhibiting system comprised of at least one corrosion inhibiting compound selected from a group of corrosion inhibiting compounds consisting of azoles, insoluble ferric pyrophosphate, soluble ferric pyrophosphate, ferrous oxalate, ferric citrate, ferrous sulfate, ferric ammonium citrate, insoluble ferric orthophosphate, soluble ferric orthophosphate, ferric ammonium oxalate, ferric ammonium sulfate, ferric bromide, ferric sodium oxalate, ferric stearate, ferric sulfate, ferrous acetate, ferrous ammonium sulfate, ferrous bromide, ferrous gluconate, ferrous iodide, ferric acetate, ferric fluoroborate, ferric hydroxide, insoluble ferric oleate, ferrous fumarate, ferrous oxide, ferric lactate, ferric resinate, and any combination thereof. Generally, the corrosion inhibiting system is present in a minor amount effective to substantially reduce the corrosiveness of the fire retardant composition.

In accordance with the present invention, the corrosion-inhibited fire retardant of the invention includes a fire retardant comprised of at least one ammonium polyphosphate.

Ammonium polyphosphate is also referred to as polyammonium phosphate and may include both ortho- and polyphosphate, other ammonium phosphates such as pyro- and metaphosphates, the alkali metal equivalents thereof, as well as a blend of phosphate polymers.

The ammonium polyphosphate solutions that are used as agricultural fertilizer and wildland (vegetative) fire retardants are manufactured by neutralizing aqueous solutions of wet-process phosphoric acid, generally containing about 68% to about 74% phosphorus pentoxide with anhydrous ammonia in such a manner that both high temperature and pressure are experienced. When prepared in this manner, a portion of the impure orthophosphoric acid polymerizes or condenses, resulting in the formation of pyrophosphate, short chain polyphosphates and, in most instances, small amounts of cyclic or metaphosphates. That portion of the acid which does not polymerize, of course, remains as orthophosphoric acid. Ammoniation of this mixture of phosphate species occurs within the reactor, as well, resulting in an aqueous solution containing ammonium ortho, pyro, tripoly, tetrapoly and some higher chain and cyclic phosphate species. These condensed phosphates generally exhibit increased water solubility as compared to orthophosphates and, consequently, more highly concentrated solutions can be prepared when they are present. The relative concentrations of the various species depends primarily on the temperature and pressure achieved within the reactor. Commercial solutions generally contain from about 34% to about 37% phosphorus pentoxide. Phosphorus pentoxide concentrations above about 37% approach water solubility limits resulting in solutions that are not stable, from which solids may precipitate during ambient temperature storage. Solutions of this type are generally referred to as either 10-34-0 or 11-37-0 liquid concentrates; the numerical designation refers to the percentage of their plant nutrient composition, i.e., ammoniacal nitrogen, phosphorus pentoxide and potassium oxide.

It should be noted that the condensed phosphates which are present in liquid concentrate solutions are subject to hydrolyses which results in de-polymerization. The rate of

hydrolytic degradation increases with time, temperature and the relative acidity of the solution. Therefore, ammonium polyphosphate concentrates and their solutions may vary in species composition as received and as time progresses during their subsequent storage.

These liquid concentrates may additionally contain small amounts of diammonium sulfate and a host of metal and alkali-metal impurities. The quantity and quality of these impurities vary with the composition of the phosphate ore, the utilized process and the extent of purification that is conducted during manufacture of the wet-process phosphoric acid. Since these solutions are manufactured primarily as nutrients, the quality control parameters of greatest interest are the percentages of their contained nutrients - nitrogen and phosphorus - and the clarity, stability and color of the solution rather than purity per se.

The corrosion inhibiting system of the invention is comprised of at least one corrosion inhibiting compound selected from a group consisting of azoles, insoluble ferric pyrophosphate, soluble ferric pyrophosphate, ferrous oxalate, ferric citrate, ferrous sulfate, ferric ammonium citrate, ferric orthophosphate, ferric orthophosphate, ferric ammonium oxalate, ferric ammonium sulfate, ferric bromide, ferric sodium oxalate, ferric stearate, ferric sulfate, ferrous acetate, ferrous ammonium sulfate, ferrous bromide, ferrous gluconate, ferrous iodide, ferric acetate, ferric fluoroborate, ferric hydroxide, ferric oleate, ferrous fumarate, ferrous oxalate, ferrous oxide, ferric lactate, ferric resinate, and any combination thereof. In one preferred embodiment, the corrosion inhibiting system is comprised of at least one soluble corrosion inhibiting compound and at least one insoluble corrosion inhibiting compound. The combination of such soluble and insoluble corrosion inhibiting iron containing compounds appears to provide the optimum combination of corrosion inhibition.

A minor amount of the corrosion inhibiting system of the invention effective to substantially reduce the corrosiveness of the fire retardant composition is included in the corrosion-inhibited fire retardant composition of the invention. A minor effective amount of

the corrosion inhibiting system is that amount which substantially reduces the corrosivity of the fire retardant. As is understood by one of ordinary skill in the art, what constitutes a substantial reduction in corrosivity is largely dependent on the specific fire retardant used in the fire retardant composition of the invention, as well as the specific composition of the corrosion inhibiting system and can be readily determined without undue experimentation.

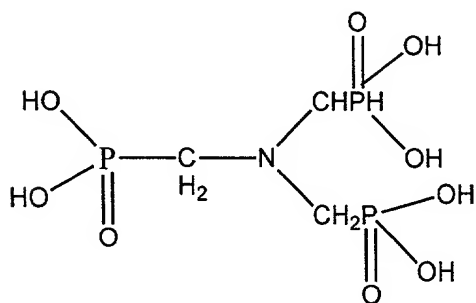
In one embodiment, the corrosion inhibiting system of the invention is present in a minor amount effective in the corrosion-inhibited fire retardant composition, in concentrate, to obtain at least one of a maximum corrosivity of aluminum to 5.0 mpy, yellow brass to 5.0 mpy, and steel to 5.0 mpy, as determined by the "Uniform Corrosion Test" set forth in Section 4.5.6.1.2 of "Specification 5100-304b (January 2000) Superseding Specification 5100-304a (February 1986)," entitled "Specification For Long Term Retardant, Wildland Fire, Aircraft or Ground Application," issued by the USDA.

In a specific embodiment, the corrosion inhibiting system of the invention comprises in the range of about .01% to about 10.0% of the total corrosion-inhibited fire retardant. In another specific embodiment, the corrosion inhibiting system of the invention comprises in the range of about 0.3% to about 6.0% of the total corrosion-inhibited fire retardant. In yet another specific embodiment, the corrosion inhibiting system of the invention comprises in the range of about 0.6% to about 5.0% of the total corrosion-inhibited fire retardant.

It has been discovered that when low concentrations of novel water soluble phosphonates are mixed with neat, ammonium polyphosphate type fire retardants, both in concentrate and its diluted solution, corrosion rates are reduced significantly. Phosphonates, also referred to as phosphonic acids, are multi-functional metal ion control agents. By definition, they contain at least one functional group, PO_3H_2 , attached to a carbon atom. Phosphonates are generally strongly negatively charged, stable in aqueous systems, high temperature, pressure and pH extremes, highly soluble in aqueous systems, and compatible

with other compounds. Although phosphonates do not readily biodegrade in continuous activated sludge tests, they disappear rapidly in the environment by a combination of photolytic and biological degradation steps. Further, phosphonates appear to possess no acute toxicological properties, which would require special handling that would differ from any strong industrial acid. The novel water soluble phosphonates suitable for use in the present invention include aminotri(methylenephosphonic acid), 1-hydroxyethylidene-1,1-diphosphonic acid, hexamethylenediaminetetra(methylenephosphonic acid), diethylenetriaminepenta(methylenephosphonic acid), and salts thereof. As one skilled in the art should readily recognize, mixtures of these novel phosphonates, and their salts, are suitable for use in the present invention. The phosphonates of the present invention are readily commercially available from Monsanto Chemical Company in St. Louis, MO, and may also be manufactured by one skilled in the art using known methods.

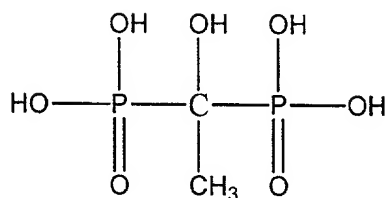
In a specific embodiment of the invention, aminotri(methylenephosphonic acid), also known as ATMP or AMP, is employed in the present invention. ATMP is represented by the following structure:



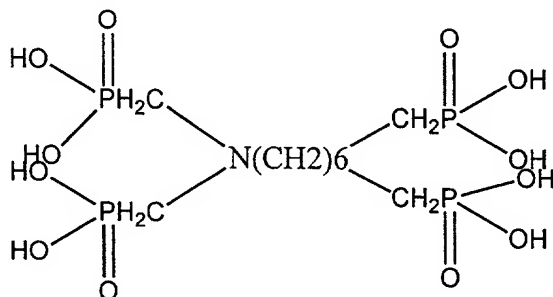
The pentasodium salt of ATMP, also referred to as Na₅ATMP, is also suitable for use in the present invention.

In yet another embodiment, 1-hydroxyethylidene-1,1-diphosphonic acid, also referred to as HEDP, is employed in the present invention. The tetrasodium salt of HEDP, also referred to

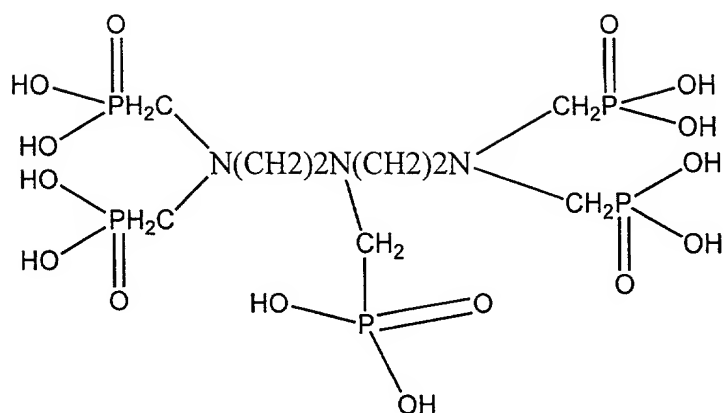
as Na₄HEDP, is also suitable for use in the present invention. HEDP is represented by the following structure:



In a further embodiment of the invention, hexamethylenediaminetetra(methylenephosphonic acid), also referred to as HDTMP, is employed in the present invention. The hexapotassium salt of HDTMP, also referred to as K₆HDTMP, is also suitable for use in the present invention. HDTMP is represented by the following chemical structure:



In still a further embodiment of the invention, diethylenetriaminepenta(methylenephosphonic acid), also referred to as DTPMP, is employed. The hexasodium salt thereof, also known as Na₆DTPMP is also suitable for use in the present invention. DTPMP is represented by the following chemical structure:



The concentrated fire retardant compositions of the invention are generally comprised of less than about 10% of at least one above-described phosphonate, based on the total ammonium polyphosphate composition, by weight. This is equivalent to about 2.3% active content in the concentrated fire retardant compositions. In one embodiment the concentrated fire retardants of the invention comprise in the range of about 1% to 10% (.23% - 2.3% active), by weight, of at least one above-described phosphonates. In a specific embodiment, the concentrated compositions of the invention are comprised of about 4.35% (1.0% active content), by weight, of at least one above-described phosphonate.

The fire retardant compositions of the invention also contain at least one suspending agent. Suspending agents effectively reduce the rate of separation and settling during long term storage. Thus, as one skilled in the art would appreciate, the amount of suspending agent depends upon its relative effectiveness per unit applied, the desired length of storage, and the additional additives incorporated into the compositions of the invention. Suspending agents useful in the compositions of the invention include colloidal clays, for example, Attapulgis, Fuller's earth, Sepiolite, Montmorillonite, and Kaolin clays. As used herein, Attapulgis clay

includes, but is not limited to attapulgite and polygorskite. As used herein, Kaolin clay includes, but is not limited to Kaolinite, $[\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2(\text{H}_2\text{O})]$ and $[\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2(\text{H}_2\text{O})]$.

As will be apparent to those skilled in the art, the fire retardants of the invention may contain or be mixed with other functional components or additives such as coloring agents, surfactants, stabilizers, opacifying agents, rheological modifying agents, any combination thereof, or with other functional components suitable coloring agents include, but are not limited to both fugitive and non-fugitive coloring agents and pigments, extenders, opacifying pigments, and other highly colored coloring agents. Rheological modifying agents suitable for use include, but are not limited to guar gum, derivatized guar gum and xanthan gum.

For example, and in one embodiment of the invention, the corrosion-inhibited fire retardant composition of the invention includes at least one highly colored pigment. The colored pigment is incorporated to assist in the visual identification of treated and untreated vegetation. Suitable highly colored pigments include iron oxide, which produces many colors like brown and red, titanium dioxide pigments, which produce a white color, or an ultra-violet sensitive dye dispersed in biodegradable plastic. However, for certain uses, like along roadsides or in parks, it may be desirable to exclude colorant from the mixture. Accordingly, as one skilled in the art would appreciate, the amount of colorant or pigment incorporated into the compositions of the invention depends on the degree of dilution and visibility contemplated by the user. Visibility is usually obtained with red iron oxide when it is present in the diluted solution in the range of about 0.15% to about 0.4%, depending on the colorant characteristics and on the vegetative and topographical characteristics of that on which it will be applied. The amount incorporated in the concentrate will, of course, vary with the dilution rate required to provide adequate fire retarding effectiveness.

In another embodiment, the present invention includes at least one of red iron oxide or brown iron oxide, or a combination thereof. In yet another embodiment, the present invention

includes a fugitive coloring agent, whose color fades upon exposure to the elements. In a further embodiment, the present invention includes opacifying pigments, which are generally not highly colored, but have the ability to cover and hide that on which it is deposited so that the highly colored pigment becomes more visible.

Surfactants may also be added to increase visibility, through the generation of a foam, and to improve penetration of the retardant solution into porous fuels. Accordingly, as one skilled in the art would appreciate, the amount and type of surfactant incorporated into the compositions of the invention depends on the degree of the dilution and visibility contemplated by the user.

It has been discovered that azoles are effective corrosion inhibitors for brass. In one embodiment of the invention, the compositions of the invention comprise at least one azole. As used herein, an azole is any of a group of chemical compounds with a five-membered ring containing one or more nitrogen atoms. Azoles suitable for use in the corrosion-inhibited fire retardants of the invention include, but are not limited to tolytriazole, benzotriazole, mercaptobenzothiazole, dimercaptothiadiazole, 1,2 benzisothiazoline-3-1, 2-benzimidazolone, 4,5,6,7-tetrahydrobenzotriazole, tolylimidazole, 2-(5-ethyl-2-pyridyl) benzimidazole, phthalimide, any alkali metal salts thereof and combinations thereof. The amount of azole or other corrosion inhibitor is dependent upon the corrodible metal for which corrosion resistance is desired, the level of resistance desired, and the specific concentration of the fire retardant composition employed, including corrosion inhibiting compounds contained therein.

The corrosion-inhibited fire retardant compositions of the inventions, adapted for application to wildland fires, are prepared in accordance with the present invention by forming an intermediate concentrate composition comprising the above-described corrosion-inhibited fire retardant compositions of the invention, and diluting the intermediate concentrate with water to form the compositions of the invention adapted for application to wildland fires. The

intermediate concentrate is formed by methods well known in the art, for example, by admixing the above-described elements comprising the fire retardant compositions of the invention using manual or mechanical mixing techniques.

To suppress wildland fires, the corrosion-inhibited fire retardant compositions of the invention are diluted with water and applied on threatened vegetation, ahead of approaching wildland fire. Ammonia from both the ammonium phosphate and the ammonium sulfate are liberated at temperatures below the ignition temperature of the fuel. The phosphoric and sulfuric acids are both initially effective fire retarding acids. The phosphoric acid will remain present and effective with the vegetative fuel until temperatures exceed 600°C. However, the boiling point of sulfuric acid is much lower and the amount present will decrease as fuel temperature increases. Thus, at least a portion of the sulfuric acid is still present at the ignition temperature of the fuel. The resultant mineral acids subsequently react with the cellulosic components of vegetative fuels on which they are applied. Their thermal decomposition is thereby altered in such a manner that they will no longer serve as fuel. These reactions are described in U.S. Pat. No. 4,839,065 to Vandersall, which is hereby incorporated by reference in its entirety.

Prior to use, and in one embodiment of the invention, the compositions of the invention are blended with water to form dilute solutions containing the amount of phosphorus pentoxide required to achieve the maximum amount of vegetation coverage at an application rate sufficient to reduce the flammability of the vegetative fuels to the desired level. The water used in the composition of the invention may be tap water or water from other convenient water sources.

In a specific embodiment, the compositions of the invention are blended with water to form dilute solutions containing the amount of phosphorus pentoxide required to meet USDA, Forest Service Specification fire-retardant effectiveness requirements. This concentration,

which is determined via combustion-retarding effectiveness testing described in USDA, Forest Service Specification 5100-304b, "4.5.2. Combustion Retarding Effectiveness Test," will generally depend on the percentage of phosphorus pentoxide present in the concentrated composition and the extent of its availability for retarding reactions. The minimum corrosivity rate specified in Specification 5100-304b is generally obtained when the fire retardant concentrate of the invention is diluted with about 1 to about 8 volumes of water.

In one embodiment, the above described fire retardant compositions are used as agricultural plant nutrients. The corrosion inhibiting system is present in a minor effective amount to substantially reduce corrosiveness of the agricultural plant nutrient. As one skilled in the art can appreciate, the effective amount varies depending on the specific plant nutrient formulated. However, one skilled in the art can readily determine the amount without undue experimentation.

A method of inhibiting corrosion using the fire retardant composition of the invention is also provided. According to the method of the invention, a corrodible material is provided and contacted with the fire retardant composition of the invention in an effective amount to substantially reduce the corrosiveness of the corrodible material. Any corrodible material may be used according to the method of inhibiting corrosion of the invention. In one embodiment, the corrodible material is one selected from a group consisting of steel, brass, aluminum and any alloy thereof. Prior to use, and in one embodiment of the invention, the fire retardant compositions of the invention are blended with water prior to or during contact with the corrodible material. The water used may be tap water or water from other convenient water sources.

In one embodiment, the corrosion inhibiting system includes at least one additive selected from a group of additives including coloring agents, surfactants, opacifying pigments, stabilizers, rheological modifying agents, and any combination thereof. Suitable coloring

agents include, but are not limited to both fugitive and non-fugitive coloring agents and pigments, extenders, opacifying pigments, and other highly colored coloring agents.

Rheological modifying agents suitable for use include, but are not limited to guar gum, derivatized guar gum and xanthan gum.

All references and patents cited herein are hereby incorporated by reference in their entireties for their relevant teachings. Accordingly, any reference cited herein and not specifically incorporated by reference is, nevertheless, incorporated by reference in its entirety as if part of the present specification.

The following examples illustrate specific embodiments of the invention without limiting the scope of the invention in any way. In each example, samples of ammonium polyphosphate fire retardant concentrates were mechanically admixed with iron containing compounds and the phosphonates described, and in some cases, with an azole. Any mechanical mixing technique that is well known in the art may be used in the present invention. The diluted fire retardant solutions are diluted with water, as indicated. The "Requirements" row illustrates the level of aluminum 2024-T3 corrosion allowed by the USDA, Forest Service Specifications 5100-304b, i.e., the maximum allowable corrosivity for product acceptance for use in wildland fire retardant compositions. The resulting samples were tested for corrosivity in accordance with USDA, Forest Service Specifications 5100-304b.

EXAMPLE 1-THE ALUMINUM CORROSIVITY OF NEAT AMMONIUM POLYPHOSPHATE SOLUTION

Table 1 illustrates the corrosion characteristics of neat, unadulterated fertilizer grade 10-34-0 and 11-37-0 ammonium polyphosphate liquid concentrates obtained from three different sources. All of the samples are either 10-34-0 or 11-37-0, as received, with no additions. The corrosivity of the samples were expressed in milli-inches per year ("mpy") of metal loss on exposed metal surface based on the conventional USDA, Forest Service

Specifications for determining corrosivity. Both the concentrated retardant and its diluted solutions were tested at each temperature and condition indicated.

The diluted solutions were prepared by admixing four to five volumes of water with one volume of the concentrated solution. Thus, the diluted solutions were in the range of between about 15% to about 20% by volume of the concentrate.

In accordance with the Forest Service Specifications for corrosion testing of fire retardants, a one-inch wide, four-inch long, one-eighth inch thick coupon of the aluminum was obtained from a standard source. The coupon is cleaned, dried and weighed according to standard USDA, Forest Service Specification Protocols and suspended in a one quart, straight sided jar filled either 50% (partially) or 100% (totally) using a piece of nylon string. When suspended in a partially full jar, the coupon was 50% (two-inches) immersed in the test solution with the other 50% extending up from the solution into the air space above it. When the jar was full with approximately 800 ml of the solution, the metal coupon was totally immersed in the solution. The jars were then closed with a screw cap and two or three identical corrosion jars (cells) of each partially and totally immersed coupons were stored at 70°F and 120°F for ninety days. At the end of the ninety day storage period, the jars were opened and the coupons were removed and cleaned according to the USDA, Forest Service Specifications. After each coupon dried it was re-weighed and its weight loss was determined by comparing its initial and final weights. The calculated weight loss and density of the metal coupon were used to extrapolate to mils (0.001 inches) of aluminum that would be lost during a one-year period at the test condition, assuming that the weight loss was experienced uniformly across the coupon surface. The corrosion rates of both the partially and totally immersed coupons were calculated using the total surface area of the coupon. The samples at each condition were then averaged and reported as the corrosion rate. The results are shown in Table 1.

Table 1

Ammonium Polyphosphate Samples	Aluminum Corrosivity when tested in the indicated configuration (mpy)										
	Neat Concentrate					Diluted Solution					
	70°F total	70°F partial	120°F total	120°F partial	70°F total	70°F partial	120°F total	120°F partial	70°F total	70°F partial	120°F total
Requirements	≤5.0	≤5.0	≤5.0	≤5.0	≤2.0	≤2.0	≤2.0	≤2.0	≤2.0	≤2.0	≤2.0
Sample 1	8.7	4.3	134.3	77.8	8.4	6.5	24.9	5.7			
Sample 2	12.4	6.6	106.6	78.5	15.2	8.4	10.1	5.6			
Sample 3			146.0				5.8				
Sample 4	8.1	4.1	140.7	67.4	5.8	6.3	11.4	7.8			
Sample 5			129.4				11.0				
Sample 6			170.0				10.8				
Sample 7			168.5				7.4				
Sample 8	10.2	5.3	165.0	88.6	12.3	6.4	21.8	13.3			
Sample 9	10.9	5.5	161.4	85.3	12.0	7.0	39.0	14.8			
Sample 10			130.0				21.1				
Sample 11			126.2				22.8				
Sample 12	4.3		109.4		11.0		6.4				
Sample 13			149.4				33.7				
Sample 14	9.5		155.6		12.7		35.8				
Sample 15	12.7	6.0	201.0	96.5	12.8	7.5	35.8	19.3			
Sample 16	13.1	7.1	159.0	86.7	11.2	6.5	42.7	21.8			
Sample 17			151.5				13.3				
Sample 18			136.3				29.2				
Sample 19	12.0	6.3	144.8	94.5	17.7	10.4	10.5	7.0			
Sample 20	9.9		115.8		13.8		12.4				
Sample 21	15.2		176.9		12.7		35.1				
Sample 22	10.9	5.5	172.6	74.8	13.1	7.2	42.9	18.3			
Average	10.6	5.6	147.7	83.3	12.2	7.4	22.0	12.6			
Range (Lo-Hi)	4.3-15.2	4.1-7.1	106.6-201.0	67.4-94.5	5.8-17.7	6.3-10.4	5.8-42.9	5.6-21.8			

The corrosivity of the ammonium polyphosphate solutions to aluminum 2024T-3 was relatively low when the temperature was maintained at about 70°F. However, none of the samples of the neat ammonium polyphosphate solutions met the Forest Service Specifications for corrosivity of fire retardants. In addition, the results show that increasing the solution temperature to 120°F dramatically increases the corrosion of the aluminum coupon by the neat ammonium polyphosphate samples, i.e., in excess of an order of magnitude.

EXAMPLE 2-THE ALUMINUM CORROSIVITY OF AMMONIUM POLYPHOSPHATE SOLUTION CONTAINING IRON OXIDE & ATTAPULGUS CLAY

The corrosion characteristics of neat fertilizer grade ammonium polyphosphate solutions containing additional amounts (<3%) of a mixture of an iron oxide colorant and Attapulugus clay is illustrated in Table 2. Each sample was prepared by admixing neat concentrated ammonium polyphosphate obtained from several sources with Attapulugus clay, and either 1.2% red iron oxide or 1.2% brown iron oxide, as indicated. In addition, 0.3% tolytriazole was also admixed into samples 11, 15, 16, 18 and 19 and 0.5% tolytriazole was admixed into sample 20. Aliquots from these concentrate samples were then diluted by admixing 1.0 volume of concentrate with 4.25 volumes of tap water. The concentrates and their solutions were then tested for corrosivity and diluted in accordance with Forest Service Specifications. The results are shown in Table 2.

Table 2

Ammonium Polyphosphate Samples	Type of Iron Oxide	Corrosion Rate (milli-inches per year)						Diluted Solution					
		Neat Concentrate			120°F			70°F			120°F		
		70°F total	70°F partial	120°F total	120°F partial	70°F total	70°F partial	120°F total	120°F partial	70°F total	70°F partial	120°F total	120°F partial
Corrosion of neat 10-34-0 Average from Table I	none	10.6	5.6	147.7	83.3	12.2	7.4	22.0				22.0	12.6
Requirements		≤5.0	≤5.0	≤5.0	≤5.0	≤2.0	≤2.0	≤2.0		≤2.0		≤2.0	≤2.0
Sample 1	Bn Iron oxide ⁽¹⁾			1.4								4.4	
Sample 2	Bn Iron oxide ⁽¹⁾			0.7								3.7	
Sample 3	Bn Iron oxide ⁽¹⁾			1.4								2.3	
Sample 4	Bn Iron oxide ⁽¹⁾			6.4								10.1	
Sample 5	Rd Iron oxide ⁽²⁾	4.6	3.6	7.3	5.0	6.7	4.4	4.0				3.6	
Sample 6	Rd Iron oxide ⁽²⁾	3.5	1.9	6.7	9.0	4.3	3.9	2.5				3.3	
Sample 7	Rd Iron oxide ⁽²⁾			2.3				4.5					
Sample 8	Rd Iron oxide ⁽²⁾	3.5	3.8	1.7	1.6	2.8	4.3	3.5				3.6	
Sample 9	Rd Iron oxide ⁽²⁾			3.0				3.1					
Sample 10	Rd Iron oxide ⁽²⁾			15.3				11.7					
Sample 11	Rd Iron oxide ⁽²⁾			32.1				7.1					
Sample 12	Rd Iron oxide ⁽²⁾			8.3				3.8					
Sample 13	Rd Iron oxide ⁽²⁾			26.3				3.9					
Sample 14	Rd Iron oxide ⁽²⁾			19.7				3.8					
Sample 15	Rd Iron oxide ⁽²⁾			4.3				0.8					
Sample 16	Rd Iron oxide ⁽²⁾			6.7				5.3					
Sample 17	Rd Iron oxide ⁽²⁾			2.3				4.2					
Sample 18	Rd Iron oxide ⁽²⁾	1.4		8.0		2.7		2.0					
Sample 19	Rd Iron oxide ⁽²⁾	5.0	3.5	8.5	13.7	5.7	4.2	5.4				4.1	
Sample 20	Rd Iron oxide ⁽²⁾	4.4	2.4	11.2	2.8	4.1	4.0	2.3				2.8	
Sample 21	Rd Iron oxide ⁽²⁾			2.0				1.9					
Sample 22	Rd Iron oxide ⁽²⁾			7.8				11.1					
Average		3.7	3.0	8.3	6.4	4.4	4.2	4.6				3.5	
Range		1.4-5.0	1.9-3.8	0.7-32.1	1.6-13.7	2.7-5.7	3.9-4.3	2.5-11.7				2.8-4.1	

(1) Brown iron oxide, Lot number 5594030A, Elementis Pigments No. 8690.

(2) Red iron oxide, Lot number 5891719A, Elementis Pigments R03097 precipitated Kroma red pigment

The results indicate that the addition of small amounts of iron oxide and clay reduce the corrosion of totally immersed aluminum in a 70°F solution by 50% to 65%. In addition, the impact of the mixture on high temperature corrosion is even more dramatic than at low temperatures. When the corrosion cell was stored at 120°F, the rate of aluminum corrosion decreased by about 75% to 90%. At both temperatures the corrosion rate on partially immersed coupons was greater than 50% of the totally immersed values, which indicated that significant interface or vapor/air phase corrosion occurs when the mixture is present in the solution. This differs from the corrosivity of the neat ammonium polyphosphate solutions of Table 1. However, the addition of 1.2% insoluble iron oxide and a clay to the ammonium polyphosphate samples did not reduce the aluminum 2024-T3 corrosion rate of the concentrates or its solutions to within the limits required by the USDA, Forest Service Specifications.

EXAMPLE 3-THE ALUMINUM CORROSIVITY OF AMMONIUM POLYPHOSPHATE SOLUTIONS CONTAINING A MIXTURE OF SOLUBLE AND INSOLUBLE IRON COMPOUNDS

The data in Tables 3a and 3b illustrate the relative effectiveness of a number of corrosion inhibitor systems containing water soluble and water insoluble sources of iron, and mixtures thereof, in several sources and types of ammonium polyphosphate concentrates and their diluted solutions. The samples were prepared by admixing either 10-34-0 or 11-37-0 type ammonium polyphosphate solutions from various sources with varying concentrations of insoluble red iron oxide or brown iron oxide additives and Attapulugus clay additives and varying the concentrations of other iron containing additives, as indicated. Samples 1, 2, 3 and 4 are 10-34-0 ammonium polyphosphate concentrates from different sources. The solutions were subjected to high shear mixing in order to activate or hydrate the clay.

Each concentrate and its diluted solution was tested for aluminum corrosivity in accordance with the Forest Service Specification protocols. The results are shown in Tables 3a and 3b.

Forest Report

Table 3a

Corrosion (mpy)		Insoluble Iron Oxide Added		Other Iron Containing Additive		Fe Content		Neat Concentrate		Diluted Solution	
Ammonium Polyphosphate Sample	%	Type	(%)	Additive	% insol.	% sol	70°F Total	70°F partial	120°F total	70°F total	120°F partial
1	0.0	None	0.0	None	0.00	0.00	9.1	5.2	140.6	10.8	16
2	1.2	Iron oxide	0.0	None	0.00	0.00	3.7	3	8.3	4.4	3.5
3	0.6	Br. Iron oxide	3.0	Sol. Ferric pyrophosphate	0.42	0.35			7.4		0.5
4	0.6	Br. Iron oxide	5.0	Sol. Ferric pyrophosphate	0.42	0.58			9.0		0.6
5	1.2	Br. Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			2.2		1.0
6	1.2	Br. Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			2.2		1.0
7	1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			5.7		1.3
8	1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			10.9		2.5
9	1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			10.8		1.6
10	1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			10.3		1.5
11	1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate*	0.84	0.35	3.1	3.1	6.1	4.4	1.6
12	1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate*	0.84	0.35			118.7		1.4
13	0.6	Br. Iron oxide	0.6	Sol. Ferric citrate*	0.42	0.13			5.5		0.6
14	0.6	Br. Iron oxide	3.0	Sol. Ferric citrate	0.42	0.66			6.7		0.6
15	0.6	Br. Iron oxide	3.0	Sol. Ferric citrate*	0.42	0.66			0.9		0.5
16	1.2	Br. Iron oxide	1.8	Sol. Ferric citrate*	0.84	0.40			15.3		3.3
17	1.2	Br. Iron oxide	1.8	Sol. Ferric citrate*	0.84	0.40			46.5		2.2
18	1.2	Red Iron oxide	1.8	Sol. Ferric citrate*	0.84	0.66			1.0		0.7
19	1.2	Br. Iron oxide	3.0	Sol. Ferric citrate*	0.84	0.66			4.5		0.7
20	1.2	Br. Iron oxide	3.0	Sol. Ferric citrate	0.84	0.66			3.9		0.6
21	1.2	Br. Iron oxide	3.0	Sol. Ferric citrate	0.84	0.66			1.0		0.7
22	1.2	Br. Iron oxide	3.0	Sol. Ferric citrate	0.84	0.66			7.9		0.8
23	0.6	Br. Iron oxide	5.0	Sol. Ferric NH4 citrate	0.42	0.88			53.9		3.4
24	1.2	Red Iron oxide	1.8	Sol. Ferric NH4 citrate	0.84	0.32			1.0		3.4
25	1.2	Red Iron oxide	3.0	Sol. Ferrous sulfate*7H2O	0.84	0.60			7.5		1.3
26	1.2	Red Iron oxide	1.2/3.0	Insol./sol. Ferric pyrophosphate	1.13	0.35					
27			1.2/3.0	Insol./sol. Ferric pyrophosphate	0.29	0.35			2.0		1.2
28			1.2/3.0	Insol./sol. Ferric pyrophosphate	0.29	0.35			2.3		0.7
29			3.0/3.0	Insol./sol. Ferric pyrophosphate	0.72	0.35			5.8		1.0
30			1.2/3.0	Insol ferric pyro/sol. Fe citrate	0.29	0.66			2.1		1.2

*These compositions contain 0.3-0.5% toltryazole for brass corrosion inhibition

Table 3b

Corrosion (mpy)		Insoluble Iron Oxide Added		Other Iron Containing Additive		Fe Content		Neat Concentrate			Diluted Solution		
Ammonium Polyphosphate Sample	%	Type	(%)	Additive	% insol.	% sol.	70°F total	70°F partial	120°F total	120°F partial	70°F total	70°F partial	120°F partial
31			1.2/3.0	Insol ferric ortho/sol. Ferric pyro	0.37	0.35			3.1				1.5
32			1.2/3.0	Insol ferric ortho/sol. Ferric pyro	0.37	0.35			2.2				1.0
33			1.2/3.0	Insol/sol. Ferric ortho	0.37	0.41			1.9				2.2
34			1.2/3.0	Insol/sol. Ferric ortho	0.37	0.41			1.9				1.5
35			1.2/4.0	Insol. Fe(III) orthophosphate/sol. Fe(III) NH ₄ citrate	0.37	0.70			2.3				1.4
36			1.2/4.0	Insol. Fe(III) orthophosphate/sol. Fe(III) NH ₄ citrate	0.37	0.70			1.8				1.2
37			1.2/3.0	Insol. Fe oxalate 2H ₂ O/sol. Ferric pyrophosphate	0.37	0.35			17.0				1.9
38			1.2/3.0	Insol. Fe oxalate/sol. Fe sulfate	0.37	0.60			37.4				5.8
39	SAMPLE 2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35	1.2	0.9	10.1	5.2	3.7	3.7	1.4
40		Br. Iron oxide	3.0	Sol. Ferric citrate	0.84	0.66			0.2				0.4
41	SAMPLE 3	Br. Iron oxide	5.0	Sol. Ferric citrate	0.42	1.10			6.2				0.5
42		Br. Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.45	2.8	2.7	110.1	70.2	11.0	6.7	7.6
43		Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			33.2		6.4		0.8
44	SAMPLE 4	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35	3.7		76.5				
45	SAMPLE 5 ⁽¹⁾	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35	2.3		2.8		2.8		1.1
46		Red Iron oxide	4.0	Sol. Ferric pyrophosphate	0.84	0.46	1.8		2.8		2.6		1.8
47		Red Iron oxide	4.0	Sol. Ferric pyrophosphate	0.84	0.35	1.4		2.1		2.7		1.2
48		Red Iron oxide	3.0	Sol. Ferric pyrophosphate	1.68	0.35			4.0				2.1
49		Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			2.4				1.1
50		Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35	1.6	1.0	2.4	1.7	2.0	3.2	2.0
51		Red Iron oxide	3.0/3.0	insol./sol. Ferric pyrophosphate	1.56	0.56	0.6		5.4		1.6		0.9
52	SAMPLE 6 ⁽²⁾	Br. Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35	2.1	1.7	113.0	52.7	11.8	6.2	8.1
53		Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			21.0				5.6
54	SAMPLE 7 ⁽²⁾	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35	4.2		83.0		3.8		1.1

(1) These compositions contain 0.3-0.5% tolyltriazole for brass corrosion inhibition.

(2) Ammonium polyphosphate sample

For comparative purposes, line 1 illustrates the average corrosion characteristics of neat concentrate and dilute solutions from Sample 1, taken from Table 1. Line 2 illustrates the average aluminum corrosion rate of the concentrate and diluted ammonium polyphosphate (as illustrated in Table 2) when the neat material was admixed with small amounts of iron oxide pigment and Attapulgus clay. Samples 1-4 were 10-34-0 type ammonium polyphosphate samples obtained from various sources. Samples 5-7 were 11-37-0 type ammonium polyphosphate samples obtained from various sources.

The data in Tables 1 and 2 illustrate that corrosive attack of aluminum was most severe when exposed to the fire retardant concentrate and its solutions at elevated (120°F/49°C) temperature in the totally immersed configuration. Consequently, the evaluation of corrosion inhibiting systems stressed testing under these conditions. Periodic testing at other conditions was conducted. Lines 3 through 6 illustrate the corrosion inhibiting effectiveness of various combinations of insoluble brown iron oxide and soluble ferric pyrophosphate. The results indicate that the USDA, Forest Service Specifications for corrosivity of fire retardants are met when 1.2% of the brown iron oxide is used in conjunction with 3.0% of the soluble ferric pyrophosphate. In addition, the results indicate that lower amounts of insoluble iron oxide result in unacceptable corrosion rates in the concentrated retardant solution.

Lines 7 through 12 illustrate the effectiveness of corrosion inhibiting systems similar to those described in the preceding paragraph, except red iron oxide is substituted for brown iron oxide. The results indicate that the red iron oxide is effective in reducing the aluminum corrosion of the concentrated and diluted ammonium polyphosphate although perhaps not quite as effective as the brown iron oxide.

Lines 13-22 illustrate the corrosion inhibiting effectiveness of mixtures of insoluble iron oxide and soluble ferric citrate. The results indicate that ferric citrate is an equally effective substitute for soluble ferric pyrophosphate. In addition, the results indicate that a mixture of

brown iron oxide and 3.0% soluble ferric citrate is capable of reducing the corrosivity of the ammonium polyphosphate samples to within acceptable levels for compliance with U.S. Forest Service Specifications for corrosivity of fire retardants.

Lines 23 and 24 illustrate the use of ferric ammonium citrate as a substitute for ferric citrate. The results indicate that the soluble ferric compounds are as effective as ammonium citrate in reducing corrosion of aluminum by ammonium polyphosphate solutions.

Lines 27 through 38 illustrate the effectiveness of systems in which only uncolored soluble and insoluble iron containing compounds are used rather than the relatively highly colored persistent iron oxides. This is important where true fugitive retardants are desired, whereby the color gradually fades when exposed to natural sunlight and disappears so as not to permanently stain that on which it is applied.

Lines 26 through 38 illustrate the effectiveness of mixtures of soluble and insoluble ferric pyrophosphate. Acceptable aluminum corrosion properties are obtained when 3.0% of the former and 1.2% of the latter are used as the corrosion inhibiting system in an ammonium polyphosphate solution. The results also indicate that an increased level of insoluble ferric pyrophosphate does not further reduce the corrosivity of the concentrate.

Lines 27 through 38 illustrate the aluminum corrosion inhibiting effectiveness of mixtures of the various soluble and insoluble iron compounds. Lines 37 and 38 revealed that, although effective, the tested ferrous salts were less effective at equivalent iron addition rates as compared to the ferric compounds.

Lines 39 through 44 illustrate the aluminum corrosion inhibiting effectiveness of various soluble and insoluble iron compounds when used in conjunction with 10-34-0 ammonium polyphosphate concentrates obtained from alternative sources. These data indicate that the amount and ratio of corrosion inhibitor necessary to reduce corrosivity to an acceptable level will need to be optimized dependent on the source and characteristics thereof.

Lines 45 through 54 illustrate the aluminum corrosion inhibiting effectiveness of the subject compounds when used in various sources of 11-37-0 type ammonium polyphosphate concentrate and their diluted solutions.

EXAMPLE 4-CORROSION CHARACTERISTICS OF AMMONIUM POLYPHOSPHATE SOLUTIONS CONTAINING WATER SOLUBLE IRON COMPOUNDS

Example 4 illustrates the effectiveness of water-soluble ferric pyrophosphate, ferric citrate and ferrous sulfate as aluminum corrosion inhibitors in ammonium polyphosphate solutions. In each sample, the indicated soluble iron compounds and 1.4% Attapulgus clay were admixed with neat ammonium polyphosphate. Aliquots were subsequently drawn from the concentrate and diluted with the prescribed amount of water. The aluminum corrosivity of both the concentrated fire retardants and their diluted solutions was determined in accordance with the aforementioned Forest Service Specifications. The results of this testing is shown in Table 4.

1644809-1

Table 4

Ammonium Polyphosphate Samples	Soluble Iron Added		Aluminum Corrosion ⁽¹⁾	
	(%)	Additive	Total Fe (%)	Dilute Solution
Average Sample from Table 1	0	None	0	5.8-39.0
1	0.6	Soluble ferric pyrophosphate	0.07	1.5
2	3.0	Soluble ferric pyrophosphate	0.35	1.6
3	3.0	Soluble ferric pyrophosphate	0.35	1.2
4	3.0	Soluble ferric pyrophosphate	0.35	1.3
5	2.4	Soluble ferric citrate	0.53	2.5
6	3.0	Soluble ferric citrate	0.66	2.4
7	3.0	Soluble ferric citrate	0.66	1.1
8	3.0	Ferrous sulfates•7H ₂ O	0.60	3.1

(1) Aluminum 2024T3 coupons tested in the manner described in USDA, Forest Service specification 5100-304b. Values obtained when the corrosion cell was maintained at 120°F (50°C) for 90 days with the coupon totally immersed therein. The data is expressed in milli-inches per year.

The results indicate that both soluble ferric and ferrous iron containing salts show utility as aluminum corrosion inhibitors in ammonium polyphosphate solutions. Relatively small concentrations (0.35%) of soluble iron derived from a soluble ferric pyrophosphate decreased the corrosion rate of totally immersed aluminum exposed to 120°F solutions of the diluted fire retardant to within the USDA Forest Service Specification requirements. The data illustrate that soluble iron containing compounds are most effective in controlling the corrosivity of diluted solutions. Since the corrosivity of both the concentrate and its diluted solutions is of importance, mixtures of water soluble and water insoluble iron compounds generally provide superior performance.

EXAMPLE 5-CORROSION CHARACTERISTICS OF AMMONIUM POLYPHOSPHATE SOLUTIONS CONTAINING OTHER WATER INSOLUBLE IRON COMPOUNDS

Table 5 illustrates the effectiveness of water insoluble ferric orthophosphate, insoluble ferric pyrophosphate and ferrous oxalate as aluminum corrosion inhibitors in ammonium polyphosphate concentrates and their dilute solutions. 1.4% Attapulgus clay was mixed with the concentrated ammonium polyphosphate, with the exception of samples 6 and 7 which contained 0.7% and 2.8% Attapulgus clay, respectively. Samples 13, 18 and 24 contained, also, an insoluble iron oxide as a solution colorant. The resultant fire retardant concentrates and their dilute solutions were evaluated in terms of aluminum corrosivity in accordance with the USDA Forest Service Specification requirements. The results of the testing are shown in Table 5 below.

Table 5

	Ammonium Polyphosphate Samples	Iron Oxide Addition		Other Insol. Fe Additive		Total Fe. Content (%)	Neat Concentrate				Diluted Solution					
		%	Type	%	Additive		70°F Total	70°F partial	120°F total	120°F Partial	70°F total	70°F partial	120°F total	120°F partial		
							Corrosion Rate (milli-inches per year)									
1	Neat 10-34-0 ⁽¹⁾	0.0	None	0.0	None	0.00	9.1	5.2	140.6	79.5	10.8	6.9	16.0	9.4		
2	Sample 1	0.0	None	1.2	Ferric pyrophosphate	0.29			2.9				1.7			
3	Sample 2	0.0	None	2.4	Ferric pyrophosphate	0.58			9.4				3.7			
4	Sample 3	0.0	None	3.0	Ferric pyrophosphate	0.72			3.5				1.1			
5	Sample 4	0.0	None	3.0	Ferric pyrophosphate	0.72			6.5				2.2			
6	Sample 5	0.0	None	3.0	Ferric pyrophosphate	0.72			2.1				1.4			
7	Sample 6	0.0	None	3.0	Ferric pyrophosphate	0.72			3.6				2.1			
8	Sample 7	0.0	None	3.0	Ferric pyrophosphate	0.72			10.7				1.0			
9	Sample 8	0.0	None	2.4	Ferric pyrophosphate	0.58			5.5				6.3			
10	Sample 9	0.0	None	3.0	Ferric pyrophosphate	0.72			6.2		3.1		1.1			
11	Sample 10	0.0	None	3.0	Ferric pyrophosphate	0.72	2.4		6.2				1.3			
12	Sample 11	0.0	None	3.0	Ferric pyrophosphate	0.72			3.4							
13	Sample 12	0.0	None	3.0	Ferric pyrophosphate	0.72			3.2				2.2			
14	Sample 13 ⁽²⁾	1.2	Red Iron oxide	0.0	None	0.84	3.7	3.0	8.3	6.4	4.4	4.2	4.6	3.5		
15	Sample 14	1.2	Red Iron oxide	3.0	Ferric pyrophosphate	1.56	2.0	1.3	4.8	3.0	1.5	3.1	0.8	2.0		
16	Sample 15	1.2	Red Iron oxide	3.0	Ferric pyrophosphate	1.56	1.6		6.2		1.6		1.0			
17	Sample 16	1.2	Red Iron oxide	3.0	Ferric pyrophosphate	1.56	2.5		0.7		2.5		0.6			
18	Sample 17	1.2	Red Iron oxide	3.0	Ferric pyrophosphate	1.56	1.9	1.2	0.5	0.2	1.1	2.4	0.8	1.9		
19	Sample 18	1.2	Red Iron oxide	3.0	Ferric pyrophosphate	1.56	2.1		2.7		1.1		0.8			
20	Sample 19	0.0	None	1.2	Ferric orthophosphate	0.16			105.3				1.7			
21	Sample 20	0.0	None	1.8	Ferric orthophosphate	0.55			108.6				3.8			
22	Sample 21	0.0	None	2.4	Ferric orthophosphate	0.73			9.3				4.1			
23	Sample 22	0.0	None	3.0	Ferric orthophosphate	0.92			2.3				4.2			
24	Sample 23	1.2	Brown Iron oxide	3.0	Ferric orthophosphate	1.25			1.5				1.0			
25	Sample 24	0.0	None	1.2	Ferrous oxalate	0.37			90.0				2.7			

(1) Average values from Table 1

(2) See Table 2.

The corrosion inhibiting effectiveness of insoluble ferric pyrophosphate was shown by a comparison of the compositions containing only this component, lines 2-13, with line 1. The effectiveness was also shown by comparison with 1.2% red iron oxide, line 14. These comparisons illustrate the effectiveness of insoluble ferric pyrophosphate as an aluminum corrosion inhibitor for concentrated ammonium polyphosphate and its solutions. It was shown to be superior to red iron oxide when compared on an equal ferric iron level. Accordingly, the insoluble ferric pyrophosphate would be preferred in many applications since it is not highly colored like the conventional iron oxides, which result in highly visible and persistent discoloration of that on which it is applied. Consequently, inhibitor systems containing these components would be suitable for use in fugitive colored fire retardant formulations.

The data contained in lines 15-19 illustrate the further reduction in aluminum corrosion, which was obtained by combining iron oxide and ferric pyrophosphate in the same corrosion inhibiting system. The results indicate that several of these formulations met the USDA, Forest Service Specifications for corrosivity of aluminum in both the concentrate and dilute forms.

The data contained in lines 20 and 23 illustrates the effectiveness of insoluble ferric orthophosphate in inhibiting the corrosion of aluminum exposed to ammonium polyphosphate solutions. The results indicate that the pyrophosphate moiety may be somewhat superior to orthophosphate for inhibiting the corrosion of aluminum.

The data contained in line 24 illustrates that increasing the ferric iron content of the corrosion inhibiting system by using mixtures of ferric orthophosphate and iron oxide is also an effective way of meeting the USDA, Forest Service Specifications for corrosivity of aluminum.

The data contained in line 25 illustrates the aluminum corrosion inhibiting effectiveness of small amounts of ferrous (FeII) iron when incorporated in ammonium polyphosphate concentrates and their dilute solutions.

EXAMPLE 6-EFFECTIVENESS OF AZOLES AS CORROSION INHIBITORS IN AMMONIUM POLYPHOSPHATE FIRE RETARDANT COMPOSITIONS

Example 6 illustrates the effectiveness of azoles as yellow brass corrosion inhibitors in concentrated ammonium polyphosphate based fire retardant formulations and in their dilute solutions. Each sample was prepared by admixing 1.4% Attapulugus clay, 1.2% red iron oxide and the indicated azole corrosion inhibitor in the neat, concentrated ammonium polyphosphate. Subsequently, the concentrates were diluted with water in the manner described herein. The samples were then tested in accordance with USDA Forest Service Specification requirements.

1644809-10304

Table 6

THE IMPACT OF AZOLES ON THE CORROSION OF YELLOW BRASS EXPOSED TO CONCENTRATED AMMONIUM POLYPHOSPHATE AND ITS DILUTED SOLUTIONS.*

Corrosion Inhibitor System	Corrosion of exposed yellow brass (mpy)							
	Concentrated Retardant				Diluted Solution			
	70T**	70P	120T	120P	70T	70P	120T	120P
None	0.5	0.6	0.6	2.0	1.5	5.7	20.3	14.9
0.3% tolyltriazole			0.2				0.3	
0.5% tolyltriazole	0.0	0.1	0.1	0.1	0.0	0.0	0.0	0.0
0.25% sodium tolyl triazole***			0.2				0.1	
0.255% sodium tolyl-triazole +			0.2				0.1	
0.425% sodium tolyl- triazole+			0.2				0.1	
0.5% sodium tolyl- triazole***			0.1				0.2	
0.5% sodium triazole++	0.1	0.1	0.1	0.1	0.1	0.3	0.3	
1.0% sodium triazole++	0.1	0.1	0.1	0.1	0.1	0.1	0.1	

* 10-34-0 containing 1.4% Atapulgus clay and 1.2% red iron oxide in addition to the described inhibitor additive.

** 70 and 120 refer to the solution storage temperature in °F, T and P refer to total of partial immersion of the metal coupon in the retardant solution during storage

*** from a 50% aqueous solution of sodium tolyltriazole.

+ from an 85% aqueous solution of sodium tolyltriazole.

++ from 100% sodium triazole.

The results indicate that azoles, including both tolytriazoles and salts thereof are effective corrosion inhibitors for yellow brass in ammonium polyphosphate concentrates and solutions. These data and others included in previous Examples illustrate the advantages of using azoles in conjunction with the iron containing inhibitors of this invention to reduce both aluminum and brass corrosivity of the fire retardant compositions to within desirable limits.

EXAMPLE 7 – THE IMPACT OF PHOSPHONATES ON AMMONIUM POLYPHOSPHATE TYPE FIRE RETARDANTS

Samples of selected commercially-available phosphonates were obtained and utilized in two studies designed to determine their impact on aluminum corrosion when blended with ammonium polyphosphate type fire retardants. In the first test series (TABLE 7A), each phosphonate was introduced at 1% based on the total ammonium polyphosphate solution. In the second test series (TABLE 7B), each phosphonate was introduced at 1% based on active phosphonic acid content. The samples were blended for 15 minutes with a laboratory stirrer fitted with a 2-inch propeller blade/shaft assembly rotating at 1500-800 rpm. Each resultant solution was divided into two one-quart jars filled to 800 ml ("milliliters"). The remaining solution was diluted with 4.25 parts water per part solution by volume and divided equally into two one-quart jars. The first pair represented the test concentrate, while the second pair represented the test dilute solution. Two one-quart jars were filled to 800 ml with uninhibited ammonium polyphosphate type fire retardant and two one-quart jars were filled to 800 ml with ammonium polyphosphate fire retardant solution, and diluted with 4.25 parts water per part fire retardant solution by volume. These uninhibited ammonium polyphosphate solutions were the standards for corrosion rate comparison.

Each of the phosphonates were utilized in a second study. 1% of the phosphonic acid, based on total solution weight, was added to each ammonium polyphosphate fire retardant samples. It should be noted that "1% Tot" means 1% phosphonate, by weight; "1% Act"

means 1% phosphonic acid component, by weight. All of the samples were tested in accordance the above-described U.S. Forest Service corrosion testing procedures. "Change" is determined by comparing the range obtained from the uninhibited average plus or minus twice the standard deviation (2σ) of the solution average of interest. The results are shown in Tables 7C and 7D below.

TABLE 7A – SAMPLES CONTAINING 1% PHOSPHONATE BASED ON TOTAL AMMONIUM POLYPHOSPHATE FIRE RETARDANT

Component	A	B	C	D	E	F	G	H
Ammonium Polyphosphate	100.0	99.0	99.0	99.0	99.0	99.0	99.0	99.0
ATMP	0	1.0	0	0	0	0	0	0
ATMP, in conc.	0	0	1.0	0	0	0	0	0
Na ₅ ATMP	0	0	0	1.0	0	0	0	0
HEDP	0	0	0	0	1.0	0	0	0
Na ₄ HEDP	0	0	0	0	0	1.0	0	0
K ₆ HDTMP	0	0	0	0	0	0	1.0	0
Na ₆ DTPMP	0	0	0	0	0	0	0	1.0
TOTAL	100%	100%	100%	100%	100%	100%	100%	100%

TABLE 7B – SAMPLES CONTAINING 1% PHOSPHONATE BASED ON PHOSPHONIC ACID CONTENT

Component	A	B	C	D	E	F	G	H
Ammonium Polyphosphate	100.0	98.0	98.0	96.55	98.33	95.24	95.65	96.0
ATMP	0	2.0	0	0	0	0	0	0
ATMP, in conc.	0	0	2.0	0	0	0	0	0
Na ₅ ATMP	0	0	0	3.45	0	0	0	0
HEDP	0	0	0	0	1.67	0	0	0
Na ₄ HEDP	0	0	0	0	0	4.76	0	0
K ₆ HDTMP	0	0	0	0	0	0	4.35	0
Na ₆ DTPMP	0	0	0	0	0	0	0	4.0
TOTAL	100%	100%	100%	100%	100%	100%	100%	100%

TABLE 7C – THE IMPACT OF 1% PHOSPHONATE BASED ON TOTAL AMMONIUM
POLYPHOSPHATE FIRE RETARDANT

Description	Concentrate					Dilute				
	1 st	2 nd	Average	2 σ	Change	1 st	2 nd	Average	2 σ	Change
Uninhibited Ammonium Polyphosphate	74.1	89.7	81.9	22.0	None	5.0	5.1	5.0	0.1	None
ATMP 1% Tot	80.6	93.4	87.0	18.1	None	3.0	4.4	3.7	1.9	Decrease
ATMP, 1% in conc. Tot	104.1	78.6	91.4	36.1	None	3.8	3.6	3.7	0.2	Decrease
Na ₅ AT MP Tot	108.3	64.4	86.3	62.1	None	3.5	4.1	3.8	0.9	Decrease
HEDP 1% Tot	82.9	87.6	85.2	6.6	None	3.2	2.8	3.0	0.6	Decrease
Na ₄ HE DP Tot	86.7	78.1	82.4	12.2	None	2.9	3.1	3.0	0.3	Decrease
K ₆ HDT MP Tot	34.8	32.0	33.4	3.9	Decrease	2.2	2.7	2.4	0.6	Decrease
Na ₆ DT PMP Tot	94.0	101.6	97.8	10.8	None	3.3	3.2	3.3	0.2	Decrease

TABLE 7D – THE IMPACT OF 1% PHOSPHONATE BASED ON ACTIVE PHOSPHONIC ACID CONTENT

Uninhibited Ammonium Polyphosphate	135.2	90.8	113.0	62.7	None	4.0	3.8	3.9	0.3	None
ATMP 1% Act	151.5	125.5	138.5	36.7	None	4.3	3.3	3.8	1.4	None
ATMP, 1% in conc. Act	91.5	96.7	94.1	7.3	None	3.7	3.4	3.6	0.3	Decrease
Na ₅ AT MP Act	125.4	131.3	128.3	8.4	None	3.6	3.9	3.7	0.3	None
HEDP 1% Act	98.9	85.6	92.3	18.7	None	3.1	3.4	3.3	0.5	Decrease
Na ₄ HE DP Act	113.2	73.4	93.2	56.3	None	6.5	6.2	6.4	0.5	Increase
K ₆ HDT MP Act	32.5	40.1	36.3	10.8	Decrease	2.7	2.5	2.6	0.4	Decrease
Na ₆ DT PMP Act	122.6	127.1	124.9	6.5	None	9.8	9.0	9.4	1.2	Increase

The results indicate that the addition of 1% K₆HDTMP to ammonium polyphosphate concentrates reduced aluminum corrosion by about 60% to about 70%, dependent on use level. Accordingly, the addition of K₆HDTMP significantly impacts the corrosivity of the ammonium

polyphosphate concentrates. The addition of 1% K₆HDTMP also reduces the aluminum corrosivity of the dilute ammonium polyphosphate solutions by about 50%. The results indicate, however, that increasing the concentration of K₆HDTMP does not improve corrosion inhibition performance in these retardants.

EXAMPLE 8- AMMONIUM POLYPHOSPHATE FIRE RETARDANTS COMPRISING TOLYTRIAZOLE, ITS DERIVATIVES AND PHOSPHONATE

Samples were prepared using ammonium polyphosphate solution, attapulugus clay, red iron oxide, and K₆HDTMP, tolytriazole, or Petrolite X-8089, in the amounts indicated in Table 8 below. The dry powder additives were combined and mixed prior to addition to the ammonium polyphosphate solution. The liquid additives were added separately after the powders. After all of the ingredients were added, the mixing speed was increased from 2.5 to 6, and the samples were then allowed to mix at that speed for one hour each, with the exception of the ammonium polyphosphate solution only sample. The sample that comprised only the ammonium polyphosphate solution was stirred with a propeller blade attached to a hand drill. After mixing for one hour, the solution viscosity was determined. When the viscosity was at least 50 centipoise ("cps"), the solution was deemed ready to use, and if not, allowed to mix an additional 15 minutes and continued in this manner until acceptable viscosity was achieved. Dilute solutions were then prepared by admixing 4.25 parts tap water with 1 part concentrate, volume to volume. The results are shown in Table 8 below. It should be noted that the corrosion data presented in Table 8 are averages of duplicate samples. In addition, "70" and "120" refer to the storage temperature; while "T" and "P" refer to coupon immersion, i.e., either total or partial. Solutions that did not have coupons in them were stored at room temperature.

**TABLE 8 - AMMONIUM POLYPHOSPHATE FIRE RETARDANTS COMPRISING
TOLYTRIAZOLE, ITS DERIVATIVES AND PHOSPHONATE**

Samples	A	B	C*	D*	E*	F	G
Components	Percent in Formulation						
Ammonium Polyphosphate	100	97.4	96.4	93.05	88.7	95.9	95.9
Clay		1.4	1.4	1.4	1.4	1.4	1.4
Red Iron Oxide		1.2	1.2	1.2	1.2	1.2	1.2
K ₂ HPTMP			1.0	4.35	8.7	1.0	1.0
Tolyltriazole						0.5	
Petrolite X-8089							0.5
Concentrate Characteristics							
Viscosity (CPS)	40	60	70	58	50	67	59
Corrosion							
Aluminum							
70T	12.4	4.6	2.4	4.7	5.5	4.5	5.1
70P	6.6	3.6	2.1	2.9	4.7	2.9	3.2
120T	106.6	7.3	4.7	4.6	4.3	7.7	8.5
120P	78.5	5.0	26.16	6.6	4.6	5.1	6.3
Yellow Brass							
70T	0.8	1.1	0.4	0.5	0.7	0.0	0.1
70P	1.0	1.1	0.4	0.5	0.6	0.1	0.2
120T	1.1	1.0	0.4	0.4	0.6	0.1	0.1
120P	2.9	1.2	1.2	1.0	1.2	0.1	0.1
Steel							
70T	2.4	4.6	1.2	1.3	2.3	1.3	1.4
70P	1.6	3.6	0.9	1.1	1.8	0.9	0.9
120T	2.1	7.3	0.9	1.0	1.2	1.1	1.1
120P	1.8	5.0	1.2	1.0	1.3	1.0	1.0
Diluted Solution Characteristics							
Viscosity (cps)	5	8	8	8	5	8	7
Corrosion							
Aluminum							
70T	15.2	6.7	5.1	4.2	5.0	4.9	5.6
70P	8.4	4.4	4.2	4.4	4.5	4.2	4.2
120T	10.1	4.0	1.8	2.4	2.4	3.1	3.1
120P	5.6	3.6	3.1	2.6	2.7	2.2	2.7
Yellow Brass							
70T	1.1	1.1	0.8	0.8	1.0	0.0	0.4
70P	4.4	4.8	4.1	3.9	4.0	0.0	0.0
120T	2.8	1.3	1.2	2.4	1.9	0.0	0.1
120P	13.5	13.9	13.7	13.0	13.6	0.0	0.1
Steel							
70T	2.3	1.8	2.1	2.7	1.8	3.4	3.9
70P	4.1	2.1	2.3	2.4	2.1	2.7	2.4
120T	1.4	0.6	0.6	0.6	0.5	1.0	1.1
120P	2.6	1.5	1.3	1.1	1.2	1.4	1.5

* Formulations C, D & E with phosphonate percent in formulation of active content; @ 1% = 0.23% act., @ 4.35% = 1.0% act., and @ 8.7% = 2.0% act.

The results indicate that the addition of clay and red iron oxide dramatically reduce the aluminum corrosion of ammonium polyphosphate concentrates, but appeared to increase the corrosion of steel in ammonium polyphosphate concentrates. K₂HDTMP appeared to have only a slightly positive effect on aluminum corrosion, although no difference was seen between

1.0 and 8.7%. The addition of half of a percentage of polytriazole had a dramatic effect on yellow brass corrosion, and reduced the corrosion to zero in the dilute solution. Petrolite® X-8089, at the same addition level, also had a significant positive impact on brass corrosion in both concentrate and dilute ammonium polyphosphate solutions.